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Process for preparing caprolactam

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PROCESS FOR PREPARING CAPROLACTAM

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The invention relates to a process for preparing caprolactam by Beckmann rearrangement of cyclohexanone oxime by feeding cyclohexanone oxime to a reaction mixture comprising (i) sulfuric acid (ii) SO_3 and (iii) caprolactam.

10 Caprolactam can be prepared by Beckmann rearrangement of cyclohexanone oxime. Such Beckmann rearrangement can be carried out by admixing cyclohexanone oxime to a reaction mixture comprising caprolactam, sulfuric acid and SO_3 . In such process the sulfuric acid and SO_3 is a catalyst for the conversion of cyclohexanone oxime towards caprolactam. Such conversion is known to occur instantaneously.

15 Such a process is for example described in US-A-3914217. In the process as described in US-A-3914217 the Beckmann rearrangement is carried out in three stages in series. Cyclohexanone oxime is fed to each stage containing a circulating rearrangement mixture having a sulfuric acid + SO_3 to caprolactam weight ratio and a SO_3 content within certain ranges. The circulating rearrangement mixture of
20 the first stage has a sulfuric acid + SO_3 to caprolactam weight ratio of 1.33 to 1.80 (molar ratio of 1.55 to 2.17) and a SO_3 content of 2 to 14 wt.%; the circulating rearrangement mixture of the second stage has a sulfuric acid + SO_3 to caprolactam weight ratio of 1.14 to 1.31 (molar ratio of 1.32 to 1.55) and a SO_3 content of at least 0.82 wt.%, preferably 0.82 to 6.5 wt.% and the circulating rearrangement mixture of the
25 third stage has a sulfuric acid + SO_3 to caprolactam weight ratio of 1.00 to 1.13 (molar ratio of 1.15 to 1.33) and a SO_3 content of at least 0.4 wt.%, preferably 0.4 to 4 wt.%. The reaction mixture obtained in the third rearrangement stage essentially containing caprolactam, sulfuric acid and optionally residual sulfur trioxide is sent to a reactor system together with ammonia, water and a solvent such as toluene. The sulfuric acid
30 and SO_3 are neutralized by converting the sulfuric acid and SO_3 into ammonium sulfate and the caprolactam is simultaneously extracted from the ammonium sulfate solution formed in this system.

It is known that rearrangement can be effected at various values for the molar ratio M. This is in particular the case for the so-called more stage
35 rearrangement in which the molar ratio M of the reaction mixture decreases in each further step. Working at low molar ratio is advantageous as it results in the formation of less ammonium sulfate during subsequent neutralization. However, it has been found

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that in the process as for example described in US-A-3914217 the yield to caprolactam is still low.

As used herein, the molar ratio M of the reaction mixture is defined as $(n_{SO_3} + n_{H_2SO_4})/n_{cap}$, wherein n_{SO_3} = quantity of SO_3 in reaction mixture, in mol (1 mol SO_3 corresponds with 80 g), $n_{H_2SO_4}$ = quantity of H_2SO_4 in reaction mixture, in mol (1 mol H_2SO_4 corresponds with 98 g) and n_{cap} = quantity of caprolactam in reaction mixture, in mol (1 mol caprolactam corresponds with 113 g). As used herein, with SO_3 content (wt.%) is meant the amount of SO_3 (g) relative to the total amount (g) of reaction mixture comprising sulfuric acid, SO_3 and caprolactam. With SO_3 is meant SO_3 which can be analyzed as such in the reaction mixture.

The object of the invention is a process for preparing caprolactam by Beckmann rearrangement of cyclohexanone oxime with an improved yield to caprolactam.

This object is achieved in that the SO_3 content of the reaction mixture is between 9 and 20 wt.% and the molar ratio M of the reaction mixture defined as $(n_{SO_3} + n_{H_2SO_4})/n_{cap}$ is between 1 and 1.4, wherein
 n_{SO_3} = quantity of SO_3 in reaction mixture, in mol
 $n_{H_2SO_4}$ = quantity of H_2SO_4 in reaction mixture, in mol
 n_{cap} = quantity of caprolactam in reaction mixture, in mol.

It has been found that with the process of the invention the yield of the rearrangement of cyclohexanone oxime to caprolactam is improved.

In the process of the invention, by-products are less produced resulting in an improved quality of the obtained caprolactam.

It has also surprisingly been found that, in spite of the high amounts of SO_3 , the caprolactam quality is not negatively influenced.

As used herein, with SO_3 content (wt.%) is meant the amount of SO_3 (g) relative to the total amount (g) of reaction mixture comprising sulfuric acid, SO_3 and caprolactam.

According to the invention, cyclohexanone oxime is introduced into a reaction mixture comprising sulfuric acid, SO_3 and caprolactam having a molar ratio of between 1 and 1.4 and a sulfur trioxide content of from 9 to 20 wt.%, preferably higher than 10 wt.% SO_3 , more preferably higher than 12 wt.% and preferably lower than 18 wt.%. Preferably, the molar ratio M of the reaction mixture is between 1.15 and 1.4 and the SO_3 content of the reaction mixture is between 9 and 20 wt.%, preferably higher than 10 wt.% and more preferably higher than 12 wt.% and preferably lower

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than 18 wt.%. As used herein, the values for M and the concentration of SO₃ and the temperature of the reaction mixture refer in particular to the values in the reaction mixture obtained after feeding of the cyclohexanone oxime into the reaction mixture. The amount of oxime introduced into such reaction mixture and the water content of the oxime introduced into such reaction mixture determines the molar ratio M and the SO₃ content of the reaction mixture obtained by admixture of cyclohexanone oxime to such reaction mixture.

The values for M and the SO₃ content may be obtained in any suitable way. In a preferred embodiment, the process is a continuous process comprising keeping the reaction mixture in circulation, feeding oleum to the circulating reaction mixture in circulation, feeding oleum to the circulating reaction mixture, and withdrawing part of the circulating reaction mixture. The amount of oleum and the SO₃ content of the oleum fed to the circulating reaction mixture may be chosen such that M and the SO₃ content of the reaction mixture have the preferred values.

Cyclohexanone oxime is preferably fed to the reaction mixture in the form of a liquid melt.

Cyclohexanone oxime (melt) and, separately therefrom, oleum are preferably introduced via dividers. Preferably cyclohexanone oxime is intensively mixed with the reaction mixture. Suitable methods for admixture cyclohexanone oxime with the reaction mixture are for example described in US-A-3601318 and EP-A-15617. In a preferred embodiment of the invention, cyclohexanone oxime is admixed to the reaction mixture using a mixing device as depicted in figure 2. In figure 2, the mixing device comprises a cylindrical tube 101 that in first part 101a narrows to throat 101b, and beyond throat 101b widens in a second part 101c. The second part 101c of the tube is connected to a second tube 102. In the throat openings 103 are present which are in connection with feed chamber 104. Cyclohexanone oxime is supplied via feed chamber 104, and fed into reaction mixture through openings 103. The mixing device comprises closures 105 with which openings 103 can be opened and closed independently. The mixing device also comprises a baffle 106 opposite to the exit of tube 101. The tube opens into collecting vessel B, having walls 110, overflow 111, and outlet 112. Reaction mixture leaving tube 102 is collected in the collecting vessel B, and leaves collecting vessel B partly via line 112 to be further circulated, and partly via overflow 111 to be fed into a subsequent reaction mixture or for the recovery of caprolactam. In a more preferred embodiment of the invention, the mixing device comprises (i) a tube through which the reaction mixture can flow, and (ii) channels

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disposed around the tube, said channels opening into the tube, said process comprising: passing the reaction mixture through the tube, and feeding the cyclohexanone oxime into the reaction mixture through one or more of said channels, wherein Re of the reaction mixture > 5000 , preferably higher than 10.000 , Re being the

5 Reynolds number as defined by $\rho \cdot V \cdot D / \eta$, wherein

ρ = density (in kg/m^3) of the reaction mixture that is fed to the tube

V = velocity of the reaction mixture, V being defined as W/A , wherein W is the flow rate (in m^3/s) of the reaction mixture that is fed into the tube and A is the cross section area of the tube (in m^2) at the level where said channels open into the

10 tube.

D = diameter of the tube at the level where said channels open into the tube (in m).

η = viscosity of the reaction mixture that is fed into the tube (in $\text{Pa}\cdot\text{s}$).

The temperature at which the Beckmann rearrangement in a reaction mixture having a molar ratio of between 1 and 1.4 and a SO_3 content of between 9 and

15 20 wt.% is carried out may have any suitable value. Preferably, the temperature is between 70 and 130°C , more preferably at a temperature of between 80 and 120°C .

The Beckmann rearrangement is preferably carried out in a circulating reaction mixture comprising caprolactam, sulfuric acid and SO_3 by continuously feeding cyclohexanone oxime and, separately therefrom, oleum to the

20 circulating reaction mixture and by continuously withdrawing a portion of the circulating reaction mixture equivalent to the amount the cyclohexanone oxime and the amount of oleum introduced to the circulating reaction mixture.

Preferably, oleum is continuously introduced into the circulating reaction mixture in an amount sufficient to maintain the molar ratio M of the reaction

25 mixture between 1 and 1.4. The SO_3 content of the oleum introduced into the circulating reaction mixture is such that the SO_3 content of the circulating reaction mixture is between 9 and 20 wt.%. Preferably, one part of cyclohexanone oxime is continuously introduced into at least 10 parts of the circulating reaction mixture; more preferably, one part of cyclohexanone oxime is introduced into at least 20 parts of the

30 circulating reaction mixture.

Preferably, the cyclohexanone oxime introduced into the reaction mixture has a water content of less than 2 wt.%, more preferably less than 1 wt.% and even more preferably less than 0.1 wt.%. Feeding cyclohexanone oxime having such low water content is advantageous as it provides an effective way of obtaining a

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reaction mixture having a SO_3 content of higher than 9 wt.%, while the addition of large quantities of SO_3 is not needed. Adding cyclohexanone oxime having such water content makes it possible to perform the Beckmann rearrangement at low molar ratio and at the same time at high SO_3 content, while the addition of large quantities of SO_3 is not needed. Performing the Beckmann rearrangement at low molar ratio and low SO_3 content is advantageous since it results in that the yield to caprolactam is improved while the amount of ammonium sulfate during subsequent neutralisation is not increased (same molar ratio).

In a preferred embodiment, the rearrangement is carried out in a plurality of stages connected in series in which the molar ratio M of the reaction mixture preferably decreases in each further step. Preferably, the rearrangement is carried out in at least two and more preferably in at least three stages connected in series. Each of these stages is charged with cyclohexanone oxime, while preferably all the oleum required is charged into the first stage. Advantageously, cyclohexanone oxime is fed to each stage with an amount decreasing from stage to stage. This is advantageous as, due to the lower molar ratio in each further stage, the yield to caprolactam decreases in each further stage. Feeding cyclohexanone oxime to each stage with an amount decreasing from each stage results in that the overall high yield to caprolactam is maintained with a comparable amount of ammonium sulphate by-product formation. In a more stage rearrangement, the Beckmann rearrangement in each stage is preferably carried out in a circulating reaction mixture comprising caprolactam, sulfuric acid and SO_3 by continuously feeding cyclohexanone oxime and, separately therefrom, oleum (first stage) resp. the amount of the circulating reaction mixture withdrawn from the previous stage (if any) to the circulating reaction mixture and by continuously withdrawing an amount of the circulating reaction mixture equivalent to the amount of cyclohexanone oxime and the amount of oleum (first stage) resp. the amount of the circulating reaction mixture withdrawn from the previous stage (if any) introduced to the circulating reaction mixture and by continuously feeding said amount to the next stage (if any). In the last stage of a more stage rearrangement a portion of the circulating reaction mixture is preferably withdrawn equivalent to the amount of cyclohexanone oxime and the amount of the circulating reaction mixture withdrawn from the previous stage and introduced into the circulating reaction mixture of the last stage; from said portion caprolactam is recovered. Preferably, oleum is continuously introduced into the circulating reaction mixture of the first stage in an amount sufficient to maintain the molar ratio M of the circulating reaction mixture in at least the last stage of the more:

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- stage rearrangement between 1 and 1.4. Working at such low molar ratio and high SO₃ content in especially the last stage of a more stage rearrangement is advantageous as low molar ratios in the last stage of a more stage rearrangement results in the formation of small amounts of ammonium sulfate during subsequent neutralisation
- 5 while high amounts of SO₃ at such low molar ratio results in an improved yield to caprolactam and additionally results in an improved quality of the obtained caprolactam. The SO₃ content of the oleum introduced into the circulating reaction mixture of the first stage is such that the SO₃ content of the circulating reaction mixture in at least the last stage is between 9 and 20 wt.%. Preferably, the oleum used in such
- 10 two or three stage rearrangement has a sulfur trioxide content of from 18 to 35% by weight. Preferably, one part of cyclohexanone oxime is continuously introduced into at least 10 parts of the circulating reaction mixture; more preferably, one part of cyclohexanone oxime is introduced into at least 20 parts of the circulating reaction mixture.
- 15 In one preferred embodiment of the invention, the rearrangement is carried out in two stages connected in series. In this embodiment, caprolactam is preferably obtained by a continuous process comprising
- a) feeding (i) oleum and (ii) cyclohexanone oxime into a first circulating reaction mixture comprising caprolactam, sulfuric acid and SO₃,
- 20 b) feeding (iii) a portion of the first circulating reaction mixture and (iv) cyclohexanone oxime into a second circulation reaction mixture comprising caprolactam, sulfuric acid and SO₃, wherein the molar ratio M of the second circulating circulation reaction mixture is between 1.0 and 1.4 and the SO₃ content of the second circulation reaction mixture is between 9 and 20 wt.%, and
- 25 c) withdrawing a portion of the second circulation reaction mixture from which caprolactam is recovered.

- In such two stage rearrangement, preferably, from 60 to 95 by weight of the total amount (fed to the first and second reaction mixture) of cyclohexanone oxime and all of the oleum is fed to the first reaction mixture. The molar ratio M in the
- 30 first circulating reaction mixture is preferably maintained between 1.2 and 2.2 and the SO₃ concentration is preferably maintained between 9 and 20 wt.%, more preferably higher than 10 wt.% and even more preferably higher than 12 wt.%. The molar ratio M in the first circulating reaction mixture is more preferably maintained between 1.4 and 1.9 and the SO₃ concentration is preferably maintained between 9 and 20 wt.%, more
- 35 preferably higher than 10 wt.% and even more preferably higher than 12 wt.%. The

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molar ratio M in the first circulating reaction mixture is even more preferably maintained between 1.5 and 1.8 and the SO₃ concentration is preferably maintained between 9 and 20 wt.%, more preferably higher than 10 wt.% and even more preferably higher than 12 wt.%. The SO₃ concentration in the first circulating reaction mixture is

5 preferably lower than 18 wt.% and even more preferably lower than 17 wt.%. The temperature at which the Beckmann rearrangement is carried out in the first stage is preferably between 70 and 130°C, preferably between 70 and 120 °C. From 5 to 40 by weight of the total amount of cyclohexanone oxime (fed to the first and second reaction mixture) is preferably fed to the second reaction mixture. The molar ratio M in the

10 second circulating reaction mixture is preferably maintained between 1 and 1.4 and the SO₃ concentration is preferably maintained between 9 and 20 wt.%, more preferably higher than 10 wt.% and even more preferably higher than 12 wt.%. The molar ratio M in the second circulating reaction mixture is more preferably maintained between 1.2 and 1.4 and the SO₃ concentration is preferably maintained between 9 and 20 wt.%,

15 more preferably higher than 10 wt.% and even more preferably higher than 12 wt.%. The SO₃ concentration in the second circulating reaction mixture is preferably lower than 18 wt.% and even more preferably lower than 16 wt.%. The temperature at which the Beckmann rearrangement is carried out in the second stage is preferably between 70 and 130°C and more preferably between 80 and 120°C.

20 In an even more preferred embodiment of the invention, the rearrangement is carried out in three stages connected in series. In this embodiment, caprolactam is obtained by a continuous process comprising

a) feeding (i) oleum and (ii) cyclohexanone oxime into a first circulation reaction mixture comprising caprolactam, sulfuric acid and SO₃,

25 b) feeding (iii) a portion of the first circulation reaction mixture and (iv) cyclohexanone oxime into a second circulation reaction mixture comprising caprolactam, sulfuric acid and SO₃,

c) withdrawing a portion of the second circulation reaction mixture,

d) feeding (v) a portion of the second circulation reaction mixture and (vi)

30 cyclohexanone oxime into a third circulation reaction mixture comprising caprolactam, sulfuric acid and SO₃, wherein the molar ratio M of the third circulation reaction mixture is between 1.0 and 1.4 and the SO₃ content of the third circulation reaction mixture is between 9 and 20 wt.%, and

e) withdrawing a portion of the third circulation reaction mixture from which

35 caprolactam is recovered.

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In such three stage rearrangement, preferably, from 60 to 95 by weight of the total amount of cyclohexanone oxime (fed to the first, second and third reaction mixture) and all of the oleum is fed to the first reaction mixture. The molar ratio M in the first circulating reaction mixture is preferably maintained between 1.2 and 2.2 and the SO_3 concentration is preferably maintained between 9 and 20 wt.%, more preferably higher than 10 wt.% and even more preferably higher than 12 wt.%. The molar ratio M in the first circulating reaction mixture is more preferably maintained between 1.4 and 1.9 and the SO_3 concentration is preferably maintained between 9 and 20 wt.%, more preferably higher than 10 wt.% and even more preferably higher than 12 wt.%. The molar ratio M in the first circulating reaction mixture is even more preferably maintained between 1.5 and 1.8 and the SO_3 concentration is preferably maintained between 9 and 20 wt.%, more preferably higher than 10 wt.% and even more preferably higher than 12 wt.%. The SO_3 concentration in the first circulating reaction mixture is preferably lower than 18 wt.% and even more preferably lower than 17 wt.%. The temperature at which the Beckmann rearrangement is carried out in the first stage is preferably between 70 and 130°C, preferably between 70 and 120 °C. From 5 to 40 by weight of the total amount of cyclohexanone oxime (fed to the first and second reaction mixture) is preferably fed to the second reaction mixture. The molar ratio M in the second circulating reaction mixture is preferably maintained between 1 and 1.6 and the SO_3 concentration is preferably maintained between 9 and 20 wt.%, more preferably higher than 10 wt.% and even more preferably higher than 12 wt.%. The molar ratio M in the second circulating reaction mixture is more preferably maintained between 1.2 and 1.4 and the SO_3 concentration is preferably maintained between 9 and 20 wt.%, more preferably higher than 10 wt.% and even more preferably higher than 12 wt.%. The SO_3 concentration in the second circulating reaction mixture is preferably lower than 18 wt.% and even more preferably lower than 16 wt.%. The temperature at which the Beckmann rearrangement is carried out in the second stage is preferably between 70 and 130°C and more preferably between 80 and 120°C. From 2 to 15 by weight of the total amount of cyclohexanone oxime (fed to the first, second and third stage) is preferably fed to the third reaction mixture. The molar ratio M in the third circulating reaction mixture is preferably maintained between 1 and 1.4 and the SO_3 concentration is preferably maintained between 9 and 18 wt.%, more preferably higher than 10 wt.% and even more preferably higher than 11 wt.%. The molar ratio M in the third circulating reaction mixture is more preferably maintained between 1 and 1.3 and the SO_3 concentration is preferably maintained between 9 and

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18 wt.%, more preferably higher than 10 wt.% and even more preferably higher than 11 wt.%. The SO₃ concentration in the third circulating reaction mixture is preferably lower than 17 wt.% and even more preferably lower than 16 wt.%. The temperature at which the Beckmann rearrangement is carried out in the third stage is preferably between 70 and 130°C and more preferably between 80 and 120°C.

It has been found that an effective way of performing a two stage or three stage rearrangement, in which the second and third (if any) circulating rearrangement mixture has a molar ratio M of between 1.0 and 1.4 and a SO₃ content of between 9 and 20 wt.%, is to introduce cyclohexanone oxime in said rearrangement mixture having a water content of less than 2 % by weight, preferably less than 1 wt.% water and even more preferably less than 0.1 wt.%. Using cyclohexanone oxime having a water content of less than 2 % by weight is advantageous because the use of cyclohexanone oxime with such a small amount of water results in that such a low molar ratio in combination with a high SO₃ content can be obtained without having to add high quantities of SO₃. Adding high quantities of SO₃ is disadvantageous, since, either a high SO₃ concentration in the oleum (H₂SO₄/SO₃ mixture) has to be applied, which is disadvantageous from an economical point of view and because the risk of fuming of the oleum increases and because the flowability of the oleum decreases, or, when still using a relatively low concentration of SO₃ in the oleum, high quantities of oleum has to be fed to the rearrangement mixture per quantity of oxime, which results in the formation of high amounts of by-product (ammonium sulfate) during subsequent neutralization. Introducing cyclohexanone oxime having such a low water content is advantageous as either a higher yield to caprolactam can be obtained for a given amount of SO₃ added to the process, or less SO₃ needs to be added to obtain a given yield to caprolactam. In addition, introducing cyclohexanone oxime having such a low water content is advantageous as either an improved quality of the obtained caprolactam can be obtained for a given amount of SO₃ added to the process, or less SO₃ needs to be added to obtain a given yield to caprolactam.

One way of obtaining cyclohexanone oxime having a water content of less than 2 wt.% is drying cyclohexanone oxime with a high water content for example with inert gas. A preferred way of obtaining cyclohexanone oxime having a water content of less than 2 wt.% is a process in which cyclohexanone oxime is obtained by

- preparing an organic medium comprising cyclohexanone oxime dissolved in an organic solvent, and
- separating, by distillation, cyclohexanone oxime from said organic medium.

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Preparing an organic medium comprising cyclohexanone oxime dissolved in an organic solvent is preferably carried out by contacting in a reaction zone in countercurrent flow a stream of a solution of cyclohexanone in an organic solvent which is also a solvent for the cyclohexanone oxime and a stream of an a
5 phosphate buffered, aqueous solution of hydroxylammonium; and withdrawing from the reaction zone an organic medium of cyclohexanone oxime dissolved in said organic solvent. Particularly suitable organic solvent for use in the process for preparing cyclohexanone oxime are toluene and benzene. Preferably toluene is used as organic solvent. The phosphate buffered, aqueous reaction medium is preferably continuously
10 recycled between a hydroxylammonium synthesis zone and a cyclohexanone oxime synthesis zone. In the hydroxylammonium synthesis zone hydroxylammonium is formed by catalytic reduction of nitrate ions or nitric oxide with hydrogen. In the cyclohexanone oxime synthesis zone, hydroxylammonium formed in the hydroxylammonium synthesis zone reacts with cyclohexanone to form cyclohexanone
15 oxime. The cyclohexanone oxime can then be separated from the aqueous reaction medium which is recycled to the hydroxylammonium synthesis zone. An organic medium comprising the formed cyclohexanone oxime dissolved in said organic solvent is withdrawn from the reaction zone, and distilled to recover cyclohexanone oxime having a water content less than 1 wt.% and even less than 0.1 wt.%.

20 The recovery of caprolactam from the reaction mixture obtained in the last stage of the Beckmann rearrangement may be performed by known methods. Preferably, the reaction mixture obtained in the last stage of the Beckmann rearrangement is neutralized with ammonia in water and the ammonium sulfate thus formed is removed from the caprolactam solution. The caprolactam solution may be
25 purified by known procedures.

Description of preferred embodiment

Figure 1 shows a preferred set-up for a rearrangement in three stages comprising a first circulation system, a second circulation system and a third
30 circulation system. The first circulation system comprises mixing device A1, collecting vessel B1, pump C1 and cooler D1, and a first reaction mixture is kept in circulation via line 1. The second circulation system comprises mixing device A2, collecting vessel B2, pump C2 and cooler D2, and a second reaction mixture is kept in circulation via line 11. The third circulation system comprises mixing device A3, collecting vessel B3,
35 pump C3 and cooler D3, and a third reaction mixture is kept in circulation via line 21.

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Cyclohexanone oxime and oleum are fed into the first reaction mixture via line 2 and line 3 respectively. A portion of the first reaction mixture is withdrawn from collecting vessel B1 via line 4 and fed into the second reaction mixture. Cyclohexanone oxime is fed into the second reaction mixture via line 12. A portion of the second reaction mixture is withdrawn from collecting vessel B2 via line 14 and fed into the third reaction mixture. Cyclohexanone oxime is fed to the third reaction mixture via line 24. A portion of the third reaction mixture is withdrawn from collecting vessel B3 via line 34. The process is carried out continuously.

Figure 2 shows a mixing device that is preferably used as mixing device A1, mixing device A2, and mixing device A3.

The following specific examples are to be construed as merely illustrative, and not limitative, of the remainder of the disclosure.

In the examples the yield to caprolactam was determined as follows: Samples were taken from the reaction mixture leaving the last stage of the rearrangement. The yield (amount of caprolactam formed per amount of cyclohexanone oxime fed to the reaction mixture) was determined as follows: To a first part (0.2 g) of each sample concentrated sulfuric acid (20 ml, 96wt%) was added, as well as 15 g K₂SO₄ and 0.7 g HgO. The nitrogen content of the resulting acidic mixture was determined using the Kjeldahl Method, from which the molar concentration of nitrogen in the first part of the sample (TN) was calculated. A second part of each sample is extracted with chloroform. This method is based on the fact that caprolactam enters the chloroform phase. The impurities stay in the water phase. The extracted aqueous phase is analyzed for its nitrogen content by the Kjeldahl Method, from which the molar concentration of nitrogen in the second part of the sample (RN) was calculated. The yield is calculated as follows:

$$\% \text{ yield} = \left(1 - \frac{RN}{TN}\right) \times 100$$

The absorbance at 290 nm (E_{290}), used as quality specification of the obtained caprolactam, was determined as follows:

The reaction mixture leaving the last stage of the rearrangement was neutralized with ammonia, and the resulting caprolactam-containing aqueous phase was separated. The absorbance of the separated caprolactam-containing aqueous phase was measured at a wavelength of 290 nm using a 1 cm cuvette (calculated for a 70 wt. %

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aqueous caprolactam solution).

Examples I-V

- In a laboratory setup, in a 0.5 l baffled reactor equipped with a turbine type stirrer, cyclohexanone oxime (containing less than 100 ppm water) and oleum were continuously added to a reaction mixture comprising caprolactam, sulfuric acid and sulfur trioxide and reaction mixture is continuously withdrawn. The amount of reaction mixture withdrawn is equivalent to the amount of cyclohexanone oxime and oleum introduced into the reaction mixture. Cyclohexanone oxime was intensively mixed with the reaction mixture. In each experiment the molar ratio M of the reaction mixture was kept around 1.2. The temperature at which the experiments were performed was 95°C. The SO₃ content (%SO₃) of the reaction mixture was varied from 5 to 15% by using oleum with different SO₃ content. The results are given in Table I. Table I below shows that at a given molar ratio the yield to caprolactam increases and the quality improves at increasing SO₃ amount in the reaction mixture.

Table I

%SO ₃	Yield	Extinction at 290 nm (1 cm/70wt.%)
4.5	97.73	3.7
6.7	97.95	3.2
9.4	98.21	2.50
13.6	98.51	1.42

Examples VI-X

- Examples I-V were repeated with the difference that the temperature at which the experiments were performed was 75°C. The results are given in Table II. Table II below shows that at a given molar ratio the yield to caprolactam increases and the quality improves at increasing SO₃ amount in the reaction mixture.

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Table II

%SO ₃	Yield	Extinction at 290 nm (1 cm/70wt.%)
3.4	97.66	2.8
6.3	97.85	2.2
9.9	98.23	1.27
15.2	99.04	0.3

Example XI

A set-up was used as depicted in figures 1 and 2. To the 1st step of a rearrangement system 7.1 t/hr oxime containing less than 100 ppm water is fed (2) and 9.8 t/hr oleum containing 29 wt.% SO₃ (3). The temperature in the reactor is maintained at 102°C by circulating the rearrangement mixture at a rate of 400 t/hr over a cooler (D1) in which its temperature is lowered to 77°C. The oxime is mixed into the circulating mixture through a mixing device (A1) having a throat diameter of 51 mm (101b) and the mixing device was provided with 16 channels (diameter 3 mm). Cyclohexanone oxime was fed through 8 channels (8 of the channels being in closed position). The velocity of the circulating mixture in the throat is 40 m/s and the velocity at which cyclohexanone oxime is fed to the circulating reaction mixture is 41 m/s. The reactor discharge (4) is sent to the 2nd step of the rearrangement system where 1.9 t/hr oxime of identical origine is added (12). In the second and third step of the rearrangement system the oxime is mixed into the circulating mixture through a mixing device (A1) as used in the first step but of which the dimensions are adapted to the lower throughput in the second and third step. Circulation rate is 150 t/hr and cooler (D2) outlet temperature is 72°C and the reactor operates at 86 °C. Finally the discharge of the 2nd reactor (14) is sent to the 3rd step of the rearrangement system where 1.1 t/hr oxime is added (22). Operating temperature is again 86 °C controlled by circulating rate of 100 t/hr and cooler (D3) outlet temperature of 76°C.

The molar ratio M of the reaction mixture in the third step is 1.19. The SO₃ content of the reaction mixture in the third step was 14.3 wt.%. The yields in the discharge of each rearrangement reactor were determined using the above given method. These yields are overall yields and through calculation the yield of the second and third step is determined. The overall yield of the 3-step rearrangement system was 99.5 %. The yield of the third step was 98.9%. The extinction at 290 nm (determined as given

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above) was 0.365.

Comparative Experiment A

Example XI was repeated with the difference that cyclohexanone
5 oxime with 4.5 wt.% water was used and that 9.3 t/hr oleum containing 29 wt.% SO₃.
To ensure similar oleum to oxime consumption ratios the oleum feed was adjusted in a
way that the molar ratios measured in each of the three steps were close or identical to
the values from Example XI. The molar ratio M of the reaction mixture in the third step
is 1.20. The SO₃ content of the reaction mixture in the third step was 3.6 wt.%. The
10 yields in the discharge of each rearrangement reactor were determined. These yields
are overall yields and through calculation the yield of the second and third step is
determined. The overall yield of the 3-step rearrangement system was 98.3 %. The
yield of the third step was 98.3%. The extinction at 290 nm (determined as given
above) was 1.036.

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CLAIMS

1. Process for preparing caprolactam by Beckmann rearrangement of cyclohexanone oxime by feeding cyclohexanone oxime to a reaction mixture comprising (i) sulfuric acid (ii) SO_3 and (iii) caprolactam, wherein the SO_3 content of the reaction mixture is between 9 and 20 wt.% and the molar ratio M of the reaction mixture defined as $(n_{\text{SO}_3} + n_{\text{H}_2\text{SO}_4})/n_{\text{cap}}$ is between 1 and 1.4, wherein
5
10
 n_{SO_3} = quantity of SO_3 in reaction mixture, in mol
 $n_{\text{H}_2\text{SO}_4}$ = quantity of H_2SO_4 in reaction mixture, in mol
 n_{cap} = quantity of caprolactam in reaction mixture, in mol.
2. Process according to claim 1, wherein the molar ratio M of the reaction mixture is between 1.15 and 1.4 and the SO_3 content of the reaction mixture is between 10 and 18 wt.%.
- 15 3. Process according to any one of claims 1-2, wherein the reaction mixture is kept in circulation in a circulation system and wherein oleum is continuously introduced into the reaction mixture in an amount sufficient to maintain the molar ratio M of the reaction mixture between 1 and 1.4 and wherein the SO_3 content of the oleum introduced into the circulating reaction mixture is such that the SO_3 content of the circulating reaction mixture is between 9 and 20 wt.%.
20
4. Process according to any one of claims 1-3, wherein the cyclohexanone oxime has a water content of less than 2 % by weight.
5. Process according to any one of claims 1-4, wherein the cyclohexanone oxime has a water content of less than 1 wt.% by weight.
- 25 6. Process according to any one of claims 1-5, wherein the cyclohexanone oxime is obtained by
 - a) preparing an organic medium comprising cyclohexanone oxime dissolved in an organic solvent
 - 30 b) separating, by distillation, cyclohexanone oxime from said organic medium.
7. Process according to any one of claims 1-6, wherein caprolactam is prepared in a more stage rearrangement in which the reaction mixture of at least the last stage has a molar ratio M of between 1 and 1.4 and a SO_3 content of
35 between 9 and 20 wt.%.

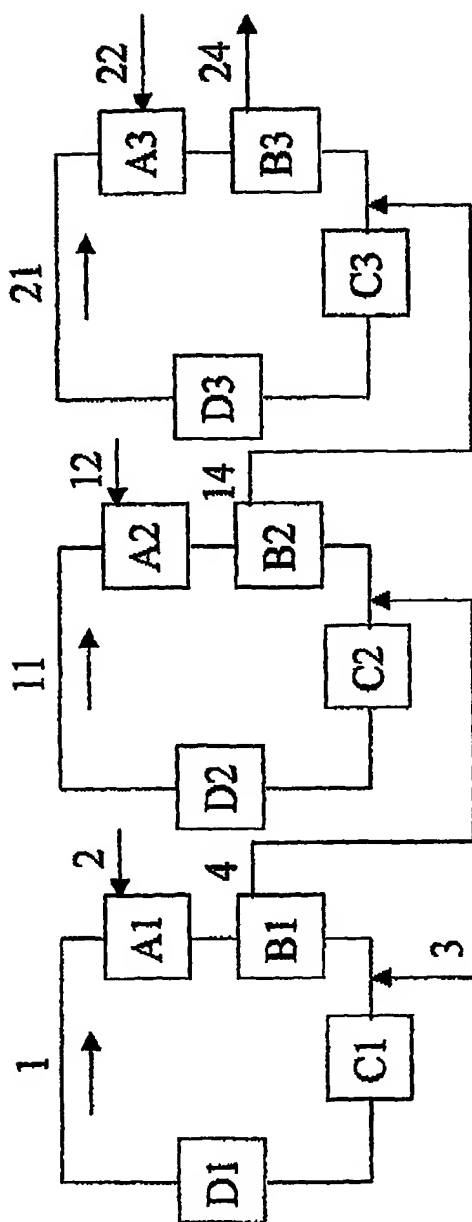
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8. Process according to any one of claims 1-6, wherein the caprolactam is obtained by a continuous process comprising
- a) feeding (i) oleum and (ii) cyclohexanone oxime into a first reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
- 5 b) feeding (iii) a portion of the first reaction mixture and (iv) cyclohexanone oxime into a second reaction mixture comprising caprolactam, sulfuric acid and SO_3 , wherein the molar ratio M of the second reaction mixture is between 1.0 and 1.4 and the SO_3 content of the second reaction mixture is between 9 and 20 wt.%,
- 10 c) withdrawing a portion of the second reaction mixture.
9. Process according to any one of claims 1-6, wherein the caprolactam is obtained by a continuous process comprising
- a) feeding (i) oleum and (ii) cyclohexanone oxime into a first reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
- 15 b) feeding (iii) a portion of the first reaction mixture and (iv) cyclohexanone oxime into a second reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
- c) withdrawing a portion of the second reaction mixture,
- d) feeding (v) a portion of the second reaction mixture and (vi) cyclohexanone oxime into a third reaction mixture comprising caprolactam, sulfuric acid and SO_3 , wherein the molar ratio M of the third reaction mixture is between 1.0 and 1.4 and the SO_3 content of the third reaction mixture is between 9 and 20 wt.%, and
- 20 e) withdrawing a portion of the third reaction mixture.
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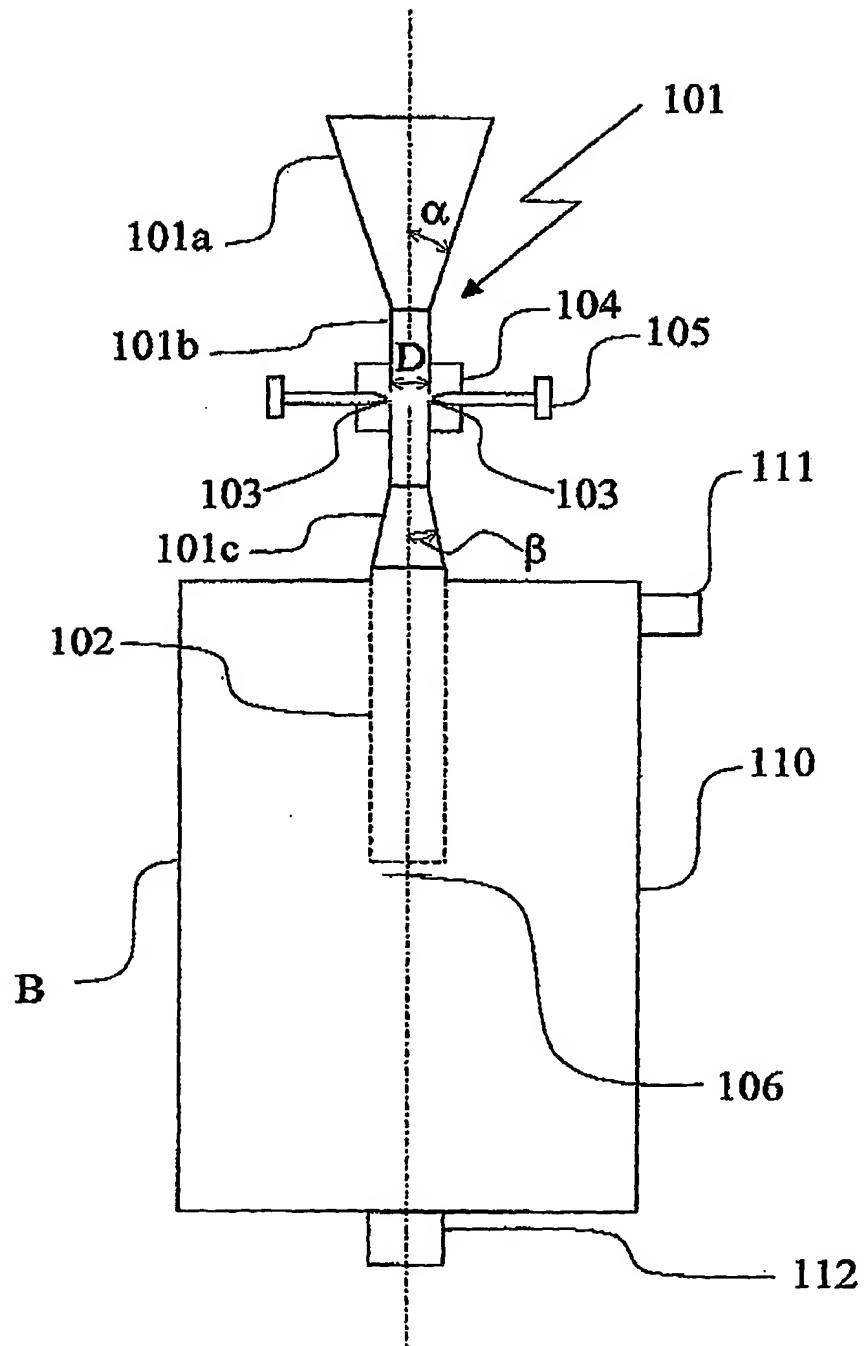
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ABSTRACT

The invention relates to a process for preparing caprolactam by Beckmann rearrangement of cyclohexanone oxime by feeding cyclohexanone oxime to
5 a reaction mixture comprising (i) sulfuric acid (ii) SO_3 and (iii) caprolactam, wherein the SO_3 content of the reaction mixture is between 9 and 20 wt.% and the molar ratio M of the reaction mixture defined as $(n_{\text{SO}_3} + n_{\text{H}_2\text{SO}_4})/n_{\text{cap}}$ is between 1 and 1.4, wherein
 n_{SO_3} = quantity of SO_3 in reaction mixture, in mol
 $n_{\text{H}_2\text{SO}_4}$ = quantity of H_2SO_4 in reaction mixture, in mol
10 n_{cap} = quantity of caprolactam in reaction mixture, in mol.



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